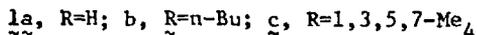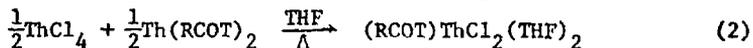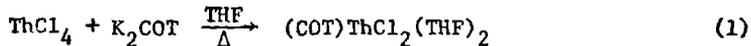# CYCLOOCTATETRAENEACTINIDE(IV) BIS-BOROHYDRIDES

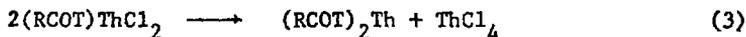Jeffrey P. Solar, Andrew Streitwieser, Jr.,
and Norman Edelstein

Materials and Molecular Research Division, Lawrence
Berkeley Laboratory, Berkeley, California 94720
and
Department of Chemistry, University of California,
Berkeley, California 94720

Although bis(η^8-cyclooctatetraene)actinide(IV) (Figure 1a) complexes have been extensively studied (1) since the synthesis of uranocene in 1968 (2,3), mono-COT actinide "half-sandwiches" (Figure 1b) were unknown until recently (4,5). The proposed co-valent bonding, involving overlap between filled ligand e_{2g} orbitals with empty metal 5f orbitals (3), could also apply to the bonding in mono-ring complexes. Whereas uranocene has been compared to ferrocene, COT half-sandwiches could show the varied reactivity exhibited by mono-cyclopentadienyl transition metal complexes such as CpFe(CO)$_2$Cl. Thus, reactions such as ligand substitution and reactions of coordinated ligands might be observed along with the usual reactions of uranocene. Mono-COT actinide complexes could also show chemistry similar to the (C$_5$Me$_5$)$_2$MX$_2$ compounds studied by Marks and coworkers (6).

The possibility of COT half-sandwich complexes was established by the observation of an intermediate COT signal in the nmr spectrum of the preparation of thorocene from ThCl$_4$ and K$_2$BuCOT (4). LeVanda and Streitwieser were able to isolate a white crystalline solid from the reaction of equimolar amounts of ThCl$_4$ and K$_2$COT (4) and an x-ray crystal structure determination (7) confirmed the product as (COT)ThCl$_2$(THF)$_2$, 1a. A better synthesis for 1a and complexes with substituents on the cyclooctatetraene ring is reaction of a thorocene and ThCl$_4$ in refluxing THF.

$$\text{ThCl}_4 + \text{K}_2\text{COT} \xrightarrow[\Delta]{\text{THF}} (\text{COT})\text{ThCl}_2(\text{THF})_2 \qquad (1)$$

$$\tfrac{1}{2}\text{ThCl}_4 + \tfrac{1}{2}\text{Th}(\text{RCOT})_2 \xrightarrow[\Delta]{\text{THF}} (\text{RCOT})\text{ThCl}_2(\text{THF})_2 \qquad (2)$$

$$\text{1a, R=H; b, R=n-Bu; c, R=1,3,5,7-Me}_4$$

Interestingly, disproportionation, e.g.,

$$2(\text{RCOT})\text{ThCl}_2 \longrightarrow (\text{RCOT})_2\text{Th} + \text{ThCl}_4 \qquad (3)$$

does not occur in this case or for $(C_5Me_5)_2MCl_2$ (8), whereas $(C_5H_5)_2UCl_2$ is apparently unstable (9). The increased stability of the pentamethylcyclopentadienyl system has been attributed to steric hindrance. The cyclooctatetraene complexes acquire two molecules of solvent (THF) to complete the coordination sphere.

In order to take advantage of the known volatility of actinide borohydride complexes (10), we sought to prepare half-sandwich borohydrides $(RCOT)M(BH_4)_2$. Several routes have been developed for the synthesis of the thorium complexes in 65 to 90% yield (5). $Th(BH_4)_4(THF)_2$ (11) has been found to react with an equimolar quantity of a cyclooctatetraene dianion in THF to give 2 as a microcrystalline white solid. In contrast to the preparation of 1, 2 is readily prepared at ambient temperature without prolonged reflux. 2 can also be prepared in a manner analogous to the synthesis of 1, using $Th(BH_4)_4(THF)_2$ and $Th(RCOT)_2$.

$$Th(BH_4)_4(THF)_2 + Th(RCOT)_2 \xrightarrow[\Delta]{THF} 2(RCOT)Th(BH_4)_2(THF)_2 \quad (4)$$

$$\begin{aligned} &2a, \ R=H \\ &b, \ R=n-Bu \end{aligned}$$
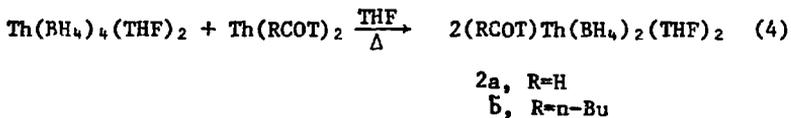
The preparation of 2 directly from $ThCl_4$ is a modification of the recent synthesis of $Cp_2U(BH_4)_2$ (12).

$$ThCl_4 + 2LiBH_4 \xrightarrow{THF} \xrightarrow{K_2COT} (COT)Th(BH_4)_2(THF)_2 \quad (5)$$
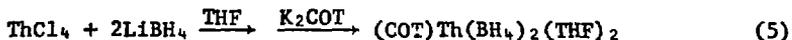
This synthesis is complicated, however, by the need to remove the LiCl formed in the reaction. In addition, metathesis of 1 with $LiBH_4$ gives the borohydride half-sandwich.

$$(RCOT)ThCl_2(THF)_2 \xrightarrow[THF]{LiBH_4} (RCOT)Th(BH_4)_2(THF)_2$$
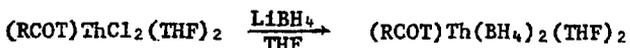
A 1,2-dimethoxyethane complex of 2, $(COT)Th(BH_4)_2(DME)$, 3, was prepared by the reaction of $Th(BH_4)_4(THF)_2$ and K_2COT in DME. In contrast to the THF complex, the DME complex is only sparingly soluble in toluene.

Although satisfactory elemental analyses have not been obtained, spectroscopic characterization of 2 is straightforward. The ^1H nmr spectrum of 2a listed in Table 1 contains signals from one cyclooctatetraene, two equivalent borohydride groups and two molecules of coordinated THF. The borohydride signal appears as a quartet due to coupling to the ^{11}B nucleus and indicates that the terminal and bridging protons are rapidly exchanging. The borohydride signal of $Cp_3Th(BH_4)$ also appears as a quartet, at δ 3.30 (13). At low temperature, the quartet of 2a collapses symmetrically to a broad singlet at δ 3.0. Marks and Shimp have observed this effect in the spectrum of $Zr(BH_4)_4$ and have interpreted the process as a temperature-dependent loss of B-H

coupling rather than a slowing of the H_t-H_b exchange (14).

The infrared spectra of 2 (Table 2) provide information regarding the binding of the borohydride group to the metal (13). Both bidentate (A) and tridentate (B) forms are known for actinide borohydrides (13,15).
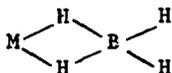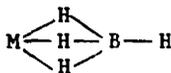

(A)   (B)

The infrared spectra of 2 are in accord with that expected for a tridentate form (B) and are similar to that from $Th[N(SiMe_3)_2]_3$ (BH_4) for which tridentate bonding has been established by X-ray crystal structure determination (16).

The infrared spectra of 2 also contain a strong band at 714 cm^{-1}; 1 gives similar spectra in this region. In thorocene, a strong absorption at 698 cm^{-1} has been assigned to a perpendicular C-H deformation (17) or, more recently, to an asymmetric ring-metal-ring vibration (18). Bands at 742 and 775 cm^{-1} in thorocene have been interpreted as C-H or C-C-C perpendicular bending modes (18). The absence of an absorption at ca 700 cm^{-1} and the presence of strong bands at 15-30 cm^{-1} higher frequency appear to be characteristic of the half-sandwich complexes.
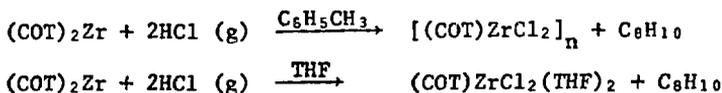
The preparation of mono-COT complexes of uranium was also of interest. Marquette-Ellis has reported an ^{1}H nmr spectroscopic study of the reaction between UCl_4, $LiBH_4$, and K_2COT (19). He observed signals from both uranocene and a second product assigned as $(COT)U(BH_4)_2$. We have studied this reaction and found that it is not straightforward. A high yield of uranocene was formed when cyclooctatetraene dianion, either solid or in THF solution, was added to a solution formed from the reaction of UCl_4 and two equivalents of $LiBH_4$. A mixture of equimolar amounts of $U(BH_4)_4$ and K_2COT also yielded uranocene upon addition of THF. However, a second product, 4, could be obtained by the slow dropwise addition of a THF solution of K_2COT to the UCl_4-$2LiBH_4$ reaction mixture. The brown product is soluble in benzene and was separated from the insoluble uranocene byproduct by filtration.

$$UCl_4 + 2LiBH_4 \xrightarrow{\text{THF, } K_2COT} (COT)U(BH_4)_2(THF)_2 + U(COT)_2$$
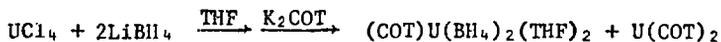
4

The visible spectrum of 4 (Table 3) contains a strong band at 396 nm and tails off to longer wavelength with a series of shoulders much like a uranocene. The infrared spectrum of the compound is nearly identical to that of the thorium analog 2a and is consistent with tridentate bonding. We are, however, unable to reproduce the nmr spectrum reported by Marquette-Ellis.

Another route to mono-cyclooctatetraene compounds is cleavage of one ring from the bis-COT complexes by protonation. Kablitz and Wilke have prepared (COT)ZrCl₂ and its THF adduct in this manner (20).

$$(COT)_2Zr + 2HCl \ (g) \xrightarrow{\ C_6H_5CH_3\ } [(COT)ZrCl_2]_n + C_8H_{10}$$

$$(COT)_2Zr + 2HCl \ (g) \xrightarrow{\ THF\ } (COT)ZrCl_2(THF)_2 + C_8H_{10}$$

Although the decomposition of uranocene in the presence of aqueous acids has been noted (3), we have found that the reaction of (BuCOT)₂Th with two equivalents of dry HCl gives 1b.

1,1'-Dibutyluranocene also reacts with HCl. The product is a dark green powder that gives a red-brown solution in THF with a visible spectrum similar to that of 3.

$$U(RCOT)_2 + 2HCl \ (g) \xrightarrow{\ THF\ } (RCOT)UCl_2(THF)_x$$

$$\underset{\sim}{5}, \ R=n\text{-}Bu$$
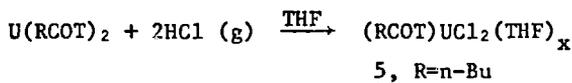
The ¹H nmr spectrum of 5 clearly shows a COT ring distinct from that of (BuCOT)₂U and, unlike a substituted uranocene, coupling is observed between the nonequivalent protons on the COT ring. Although the signals from 5 are strongly shifted by the paramagnetic uranium, the signals are much sharper than those of a uranocene. The infrared spectrum of 5 contains absorptions from the COT ring at 734 and 719 cm⁻¹, in the region expected for a half-sandwich complex. 5, however, is much less soluble than the thorium analog 2b, and unreacted uranocene can be removed by washing the mixture with benzene. LeVanda has also observed this product from the prolonged reflux of UCl₄ and U(BuCOT)₂ (21).

Several other reactions of these complexes have been investigated. Although Cp₂Zr(BH₄)₂ reacts readily with tertiary amines, converting metal-BH₄ groups to metal hydrides by formation of BH₃-amine complexes (22), (COT)Th(BH₄)₂(THF)₂ was unchanged on treatment with excess NEt₃ at room temperature. 1a was observed to react slowly with excess BEt₃ in refluxing benzene.

$$(COT)Th(BH_4)_2(THF)_2 + BEt_3 \xrightarrow[\Delta]{\ C_6H_6\ } (COT)Th(BH_3Et)_2(THF)_x$$

$$\underset{\sim}{6}$$
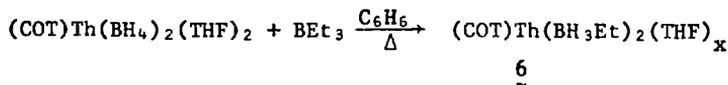
Marks and Kolb have carried out the analogous reaction of Cp₃U(BH₄) and have observed complete substitution of the terminal proton in 36 hours. In contrast, 1a was only about 50% reacted after 40 hours and a trace remained after four additional days with a fresh charge of BEt₃. The infrared spectrum of 6 is much like that of 1a but the B-H terminal absorption is absent. Neither 1a nor 6 sublime on heating in vacuo and 6 is slowly

decomposed to thorocene (and other unidentified products) at ca.
100°C at 10^{-6} torr. Thorocene is also formed when 1a is allowed
to react with K_2COT at room temperature in THF.

$$(COT)Th(BH_4)_2(THF)_2 \xrightarrow[\text{THF}]{K_2COT} (COT)_2Th$$
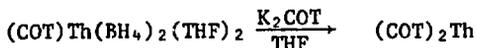
Further studies of the synthesis and reactivity of these half-
sandwich compounds are in progress.

Experimental

General. Due to the air-sensitive nature of the compounds
in this study, all work was carried out in an argon atmosphere
using a glove box or standard Schlenk techniques. Solvents were
distilled under argon from sodium-benzophenone ketyl. $LiBH_4$ was
purified by Soxhlet extraction with diethyl ether before use and
other reagent grade chemicals were used as received. Uranocenes
(3,23) and thorocenes (24) were prepared by published procedures.
$Th(BH_4)_4(THF)_2$ was prepared by a modification of the method of
Ehemann and Noth (11) using THF in place of diethyl ether and was
shown by a powder pattern to be isostructural with $U(BH_4)_4(THF)_2$
(25). The synthesis (5) and X-ray crystal structure (7) of
$(RCOT)ThCl_2(THF)_2$ have been published.
Infrared spectra were run of Nujol mulls prepared in a
glove box and sealed between salt plates. Samples could then be
transferred to a Perkin-Elmer Model 283 spectrometer without
decomposition. Visible spectra were run in stoppered glass cells
on a Cary 118 spectrometer. NMR spectra were run at 180 MHz on
a FT instrument.

Preparation of $(RCOT)Th(BH_4)_2(THF)_2$ (2). (A) $Th(BH_4)_4(THF)_2$
(0.51 g, 1.2 mmole) and K_2COT (0.21 g, 1.2 mmole) were mixed and
ca. 75 ml of THF was added. The solution was stirred in the
glove box for 16 hrs until the yellow color faded. The white
precipitate was removed by centrifugation and the solids were
washed with 10 ml of THF. The solutions were combined and the
solvent was pumped off to give 0.45 g (76%) of $(COT)Th(BH_4)_2(THF)_2$
(2a).
(B) $Th(BH_4)_4(THF)_2$ (0.37 g, 0.85 mmole) and $Th(BuCOT)_2$
(0.44 g, 0.80 mmole) were mixed and 50 ml of THF was transferred
onto the solids in vacuo. The flask was refilled with argon
and the solution was heated at reflux for 5 days. A visible
spectrum indicated no further trace of the thorocene. Removal of
the solvent in vacuo gave a light yellow solid. The residue was
rinsed with hexane and dissolved in ca. 30 ml of benzene. A small
amount of solid was removed by centrifuge and the solvent was
removed to give 0.60 g (67%) of $(BuCOT)Th(BH_4)_2(THF)_2$ (2b) as a
white solid.
(C) THF (60 ml) was added to a mixture of 1.25 g (3.3

mmole) of $ThCl_4$ and 0.16 g (7.3 mmole) of $LiBH_4$ and the solution
was stirred for 16 hrs in a glove box. A solution of 0.54 g
(3.0 mmole) of K_2COT in 40 ml of THF was added and the mixture
was stirred an additional 16 hrs. The precipitate was removed
by centrifuge and washed with two 10 ml portions of THF. The
solutions were combined and the solvent was removed. The residue
was dissolved in benzene and the insoluble material was removed
by centrifuge. Removal of the solvent gave an oily white product.
Recrystallization from benzene-hexane gave 1.38 g (91%) of
$(COT)Th(BH_4)_2(THF)_2$.

(D) $(BuCOT)ThCl_2(THF)_2$ (211 mg, 0.347 mmole) and $LiBH_4$
(36 mg, 1.6 mmole, excess) were mixed and 15 ml of THF was added.
The solution was stirred in the glove box for 2 days. The
solvent was removed and the residue was extracted with benzene.
Removal of the solvent gave $(BuCOT)Th(BH_4)_2(ThF)_2$ (2b), identi-
fied by its infrared spectrum.

Preparation of $(RCOT)Th(BH_4)_2(DME)$ (3). Following synthe-
sis A above, 0.326 g (0.725 mmole) of $Th(BH_4)_4(THF)_2$ was dissolved
in 2 ml of DME and a solution of 0.13 g (0.71 mmole) of K_2COT in
20 ml of DME was added. The solution was stirred for 40 hrs in
a glove box. The white solids were removed by centrifugation and
washed with 10 ml of DME. The solutions were combined and the
solvent was pumped off to give 0.26 g (67%) of $(COT)Th(BH_4)_2$
(DME).

Preparation of $(COT)U(BH_4)_2(THF)_x$. A solution of 0.22 g
(10 mmole) of $LiBH_4$ in 10 ml of THF was added to a solution of
1.63 g (4.3 mmole) of UCl_4 in 25 ml of THF. The solution was
stirred for 24 hrs in a glove box. K_2COT (0.75 g, 4.1 mmole)
was dissolved in 100 ml of THF and added dropwise to the UCl_4-
$LiBH_4$ solution. The resultant brown solution was stirred for
16 hrs and the solvent was pumped off. The residue was extracted
with benzene and the insoluble material was removed by centri-
fuge. The solvent was removed in vacuo leaving a brown tacky
residue. Infrared and visible spectra indicated the product to
be $(COT)U(BH_4)_2THF_x$. Recrystallization from benzene-hexane gave
a tacky brown solid.

Preparation of $(COT)Th(BH_4)_2(THF)_2$ with BEt_3. $(COT)Th(BH_4)_2$
$(THF)_2$ (0.34 g, 0.67 mmole) was dissolved in benzene and 1.7 ml
(1.7) mmole of 1 M BEt_3 in THF was added by syringe. The solu-
tion was heated at reflux for 40 hrs. The solvent was removed
and an infrared spectrum indicated that the reaction was ca. 50%
complete. Benzene and 3.0 ml of BEt_3 in THF were again added and
the solution was heated at reflux for 4 days. The solvent was
removed to give a tacky residue of $(COT)Th(BH_3Et)_2(THF)_2$.

Reaction of (COT)Th(BH$_4$)$_2$(THF)$_2$ **with** K$_2$COT. (COT)Th(BH$_4$)$_2$
(THF)$_2$ (0.253 g, 0.496 mmole) and K$_2$COT (0.089 g. 0.49 mmole)
were mixed and 50 ml of THF was added. The solution was stirred
for 3 days and the solids were removed by centrifuge. The solids
were washed with additional THF (ca. 25 ml) until no further
yellow color was extracted. The solutions were combined and the
solvent was removed to give 0.178 g (83%) of Th(COT)$_2$.

Acknowledgments

Literature Cited

1. Streitwieser, A., Jr. "Organometallic Compounds of the f-
   Elements," Marks, T.J.; Fischer, R.D., Eds. Reidel Publishing
   Co., Amsterdam (1979), 149-177.
2. Streitwieser, A., Jr.; Muller-Westerhoff, U. J. Am. Chem. Soc.
   1968, 90, 7364.
3. Streitwieser, A., Jr.; Muller-Westerhoff, U.; Sonnichsen, G.;
   Mares, F.; Morrell, D.G.; Hodgson, K.O. J. Am. Chem. Soc.
   1973, 95, 8644-8649.
4. LeVanda, C.; Streitwieser, A., Jr. Abstracts, 175th National
   Meeting American Chemical Society, Anaheim, California, March
   1978, INOR No.68.
5. LeVanda, C.; Solar, J.P.; Streitwieser, A., Jr. J. Am. Chem.
   Soc., submitted.
6. Fagan, P.J.; Manriquez, J.M.; Marks, T.J. "Organometallic
   Compounds of the f-Elements," Marks, T.J.; Fischer, R.D. Eds.
   Reidel Publishing Co., Amsterdam (1979), 113-148; and
   references therein.
7. Zalkin, A.; Templeton, D.H.; LeVanda, C.; Streitwieser, A.,
   Jr. Inorg. Chem., to be submitted.
8. Manriquez, J.M.; Fagan, P.J.; Marks, T.J. J. Am. Chem. Soc.
   1978, 100, 3939-3941.
9. Kanellakopulos, B.; Aderhold, C.; Dornberger, E. J. Organo-
   metal.Chem., 1974, 66, 447-451.
10. Schlesinger, H.I.; Brown, H.C. J. Am. Chem. Soc. 1953, 75,
    219-221.
11. Ehemann, M.; Noth, H. Z. Anorg. Allg. Chem. 1971, 386, 87-101.
12. Zanella, P.; DePaoli, G.; Bombieri, G. J. Organometal. Chem.
    1977, 142, C21-24.
13. Marks, T.J.; Kennelly, W.J.; Kolb, J.R.; Shimp, L.A. Inorg.
    Chem. 1972, 11, 2540-2546.
14. Marks, T.J.; Shimp, L.A. J. Am. Chem. Soc. 1972, 94, 1542-50.

15. Bernstein, E.R.; Hamilton, W.C.; Kiederling, T.A.; LaPlaca, S.J.; Lippard, S.J.; Mayerle, J.J. Inorg. Chem. 1972, 11, 3009-3016.
16. Turner, H.W.; Andersen, R.A.; Zalkin, A.; Templeton, D.H. Inorg. Chem. 1979, 18, 1221-1224.
17. Karraker, D.G.; Stone, J.A.; Jones, E.R., Jr.; Edelstein, N. J. Am. Chem. Soc. 1970, 92, 4841-4845.
18. Goffart, J. "Organometallic Compounds of the f-elements," Marks, T.J. and Fischer, R.D., Eds. Reidel Publishing Co., Amsterdam (1979), p. 489.
19. Marquette-Ellis, H. NATO Advanced Study Institute, Sogesta, Italy, 1979.
20. Kablitz, H.J.; Wilke, G. J. Organometal. Chem. 1973, 51, 241-271.
21. LeVanda, C. Unpublished results.
22. James, B.D.; Nanda, R.K.; Wallbridge, M.G.H. Inorg. Chem. 1967, 6, 1979-1983.
23. Streitwieser, A., Jr.; Harmon, C.A. Inorg. Chem. 1973, 12, 1102-1104.
24. LeVanda, C.; Streitwieser, A., Jr. Inorg. Chem., submitted.
25. Reitz, R.R.; Edelstein, N.M.; Ruben, H.W.; Templeton, D.H.; Zalkin, A. Inorg. Chem. 1978, 17, 658-660.

Table 1. Infrared Spectra (Nujol, cm^{-1})

Compound	$B-H_t$	$B-H_b$			COT		Other
2a (COT)Th(BH$_4$)$_2$(THF)$_2$	2482(s)	2282(w)	2220(s)	2150(m)	722(sh)	714(s)	1180(s) 1163(s)
3 (COT)Th(BH$_4$)$_2$(DME)$_2$	2464(s)	2375(w)	2282(s)	2215(s)	730(s)	716(m)	1165(s) 1120(s) 1095(m) 1038(s)
4 (COT)U(BH$_4$)$_2$(THF)$_x$	2472(s)	2339(w)	2210(s)	2142(m)	722(s)		1170 (br,s)
5 (COT)UCl$_2$(THF)$_x$					734(s)	719(s)	1135(sh) 1011(s)
6 (COT)Th(BH$_3$Et)(THF)$_2$		2310(s)	2185(s)	2128(s)			

9

Table 2. NMR Spectra (δ vs TMS)

Compound	Solvent	COT	BH_4	Other
2a $(COT)Th(BH_4)_2(THF)_2$	C_6D_6	6.69(s,8H)	3.11(q,J=85Hz,8H)	3.34,0.90(br,8H,8H,THF)
3 $(COT)Th(BH_4)_2(DME)_2$	C_6D_6	6.7(s)	3.1 (q,J=85Hz)	3.0, 2.8(DME)
5 $(BuCOT)UCl_2(THF)_x$	THF-d_8	-21.7(t,1H), -29.0(t,2H), -33.0(d,2H), -44.7(t,broad 2H)		

10

Table 3. Visible Spectra (λ_{max},nm)

4 $(COT)U(BH_4)_2(THF)_2$		396, 457, 492, 525
5 $(BuCOT)UCl_2(THF)_x$		402, 456, 499, 541